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DEPARTMENT OF COMMERCE

UNITED STATES BUREAU OF MINES
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HAFNIUM

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DEPARTMENT OF COMMERCE - BUREAU OF MINES

HAFNIUM[1]

By Paul M. Tyler[2]

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INTRODUCTION

Hafnium appears to be among the more abundant of the newly discovered elements. Though quite widely distributed in nature, its compounds chemically so resembled those of zirconium, its sister element, that it escaped detection until 1923, when Coster and Hevesy announced the discovery of the element, to which they gave the name of "hafnium", from Hafniae, the Latin name for Copenhagen, where their research work was performed. Hafnium has so far been found only as a minor constituent of zirconium minerals. Zirconium as an element was discovered more than 140 years ago, but only a few unimportant uses were found for the metal or its compounds until some 18 years ago; it is still classed among the rarer commercial metals. It is not surprising, therefore, that hafnium has not yet found a definite place for itself in industry. Nevertheless it has commanded a considerable interest among scientists; and in 1930 some 70 grams of perfectly pure oxide of hafnium were prepared in Europe. A commercial future for hafnium is already glimpsed in the radio industry, and its high melting point and electronic emissivity have already led to the taking out of patents for its use in radio tubes and incandescent electric lamp filaments and for the cathode surfaces of devices such as X-ray tubes and rectifiers.[3]

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[1] The Bureau of Mines will welcome reprinting of this article, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6457."

[2] Chief engineer, rare metals and nonmetals division, U. S. Bureau of Mines assisted by Miss E. P. Youngman of the Bureau of Mines.

Due to the fact that the separation of hafnium (compounds) from zirconium (compounds) is laborious and because of the lack of any extensive demand, hafnium compounds are expensive and not particularly easy to obtain in the market. In the United States practically none of the metal seems to be available, but hafnia (the oxide) and hafnium chloride can be purchased in small quantities at a price of approximately $25 a gram. Ores containing up to about 3 per cent of hafnia can be bought for about 50 cents a pound and ore containing 5.5 per cent may be had for $1.50 a pound.

ACKNOWLEDGMENT

In preparing the present paper, the author has depended largely upon the ratherm meager literature, references to which are given whenever possible by means of footnotes. For careful review and constructive criticism of the manuscript, and for additional information some of which has not previously been published, the author is indebted to Mr. O. Ivan Lee.

DESCRIPTION AND PROPERTIES

Hafnium is element number 72 and falls in the fourth column of the periodic system between zirconium and thorium. The atomic weight as determined by one of the discoverers is probably between 178.64 and 178.59.[4] The metal has the same crystal structure as zirconium (hexagonal) but is roughly twice as heavy. The density, according to the latest determinations by de Boer and Fast is 13.31, about the same as quicksilver and substantially heavier than lead. The atomic volume figures out to 13.42. The melting point is quite high, 2500 degrees on the Kelvin scale (about 2227° C.). According to S. Meyer,[5] hafnium is diamagnetic. The electrical resistance at 0° C. is variously given as 30×10^{-6} ohms or as 41×10^{-6} ohms, and the temperature coefficient of resistance is 0.0044 (0 - 100°).

The chemical properties of hafnium lie between those of zirconium and thorium but are much closer to, and in fact almost identical with, those of zirconium. The high melting point and light emissivity of zirconia are shared by hafnia - hafnium dioxide, HfO_2 - which may be prepared by igniting the sulphate at 1000°. The molecular volume of hafnia is 21.76, that of zirconia 21.50; and the specific gravities are 9.68 and 5.73, respectively.[6] In general any chemical reaction characteristic of zirconium is also characteristic of hafnium, although certain minor differences have been noted by Hevesy, as follows:[7]

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[3] Holst, Gilles, and Oosterhuis, Ekko, Electric Discharge Tubes with Cathode Surface of Hafnium: U. S. Patent 1701849 (to Naamlooze Vennootschap Philips' Gloeilampenfabrieken), Feb. 12, 1929: Chem. Abs., vol. 23, No. 6, Am. Chem. Soc., Mar. 20, 1929, p. 1315.

Siemens & Halske A.-G., Incandescence Cathode: Australian Patent 109083, Oct. 14, 1925; German Patent, Dec. 17, 1924; Chem. and Ind., vol. 49, No. 12, London, Mar. 21, 1930, p. 246 of Chem. Abs. sec.

Patent-Treuhand-Ges. f r Elektrische Gl hlampen, Filaments of Hafnium Carbide for Electric Lamps: British Patent 312273 (to General Electric Co., Ltd.), May 23, 1928; Chem. Abs., vol. 24, No. 4, Am. Chem. Soc., Feb. 20, 1930, p. 795.

[4] Hevesy, G., The Discovery and Properties of Hafnium: Chem. Rev., vol. 2, No. 1, Am. Chem. Soc., Apr., 1925, p. 18.

[5] Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry: vol. 7, New York, 1927, p. 170.

[6] Mellor, J. W., Work cited, pp. 170-171.

[7] Hevesy, G., The Chemistry of Hafnium: Chem. News, vol. 127, Sept. 21, 1923, London, p. 186.

> While the fluorides and double fluorides of thorium are practically insoluble, the corresponding zirconium compounds, and still more the hafnium compounds, are fairly soluble in cold, very soluble in hot, water. By this method zirconium can easily be separated from hafnium. The mineral is melted with KFHF, and by crystallizing the potassium double fluorides the hafnium concentrates in the mother liquor.
>
> Hafnium oxalate is soluble in excess of oxalic acid. The oxychloride is less soluble than zirconium oxychloride. Hafnium is more basic than zirconium; accordingly the latter is more easily precipitated by ammonia, sodium thiosulphate, etc.; and while zirconium sulphate begins to decompose above 400°, the temperature at which hafnium sulphate undergoes marked decomposition lies about 100° higher. Thorium phosphate is easily dissolved by strong acids, zirconium phosphate much less, whereas hafnium phosphate is found to be still less soluble.

It will be noted that chemically the principal difference is in basicities, and even this is too slight to afford a means for separating the two elements. Actually the only basis for effecting a separation is essentially physical and not chemical; it depends upon differences in solubilities of certain of the compounds.

OCCURRENCE

On purely theoretical grounds it is reasoned[8] that hafnium is not a very rare element. Elements that like hafnium (72) have even atomic numbers are known to be more common than nearby elements in the periodic system (Mendeleef) that have odd atomic numbers. Thus germanium (32) seems to be more abundant than gallium (31); tin (50) than indium (49); and lead (82) than thallium (81).[9] Moreover, a study of the relative abundance of the better known members of the same family in the lithosphere tends to indicate that hafnium is at least more abundant than thorium. The oxides of silicon, titanium, zirconium, and thorium are found in the earth's crust in the percentages, respectively, of 59.09, 1.05, 0.04, and 0.002.

The only known sources of potential supply of hafnium are the various zirconium minerals, notably zircon. Thorium is the higher homologue of hafnium, and it happens that zircons with relatively large thorium (or uranium) contents have been found in several cases to contain unusually large amounts of hafnium. The degree of radio-activity, in fact, is considered to be an index of the amount of hafnium present in zircon or its alteration minerals; the radioactivity is due to uranium and thorium, and hafnium is isomorphous with these elements. So far, however, no hafnium has been found in any thorium mineral.

The ratio of hafnium to zirconium in different minerals varies between wide limits. In the case of minerals associated with basic igneous rocks the ratio is rarely more than 0.02 and often less. In minerals found in acid igneous rocks, such as granites, the ratio is much higher, amounting in the case of cyrtolite (altered zircon) to 0.4 and in the case of thortveitite to 0.5. Zircon, the commonest zirconium mineral, occurs in both basic and acid rocks, but in the former association it apparently contains scarcely more than one-third as much hafnia as it does when found in acid or granitic rocks.

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[8] Lee O. Ivan, The Mineralogy of Hafnium: Chem. Rev., vol. 5 No. 19, 1928, pp. 19-20.

[9] A number of exceptions to this rule should be noted, however. Tin (50), for example, is probably less abundant than antimony (51).

List of zirconium minerals known to contain hafnium[1]
(Specific paired analyses are underscored)

Name	Per cent ZrO_2	Per cent HfO_2
Baddeleyite (distinct crystals)	96.5-97.7-98.9	1.2
Syn. Brazilite (fibrous, botryoidal, columnar)	71-93	
Syn. var. (rock) Jacupirangite (crystallized)		
(1. Favas (alluvial pebbles)	59-74-92.4	0.5-0.5-0.7
Zirconia ((Brazilite	71-93	
ore ((Zircon	67	
(2. "Zirkite" (	80-85	
(mixture) (Unnamed Zr silicate		
((orvillite?)	75	
Catapleite	31.53	0.3
Elpidite	20.28	0.2
Eudialyte	12.20-14.32	0.1-0.2-0.17
Var. Eucolite	12.21	0.2
Polymignite	29.11	0.6
Pyrochlore	2.90	Trace
Rosenbuschite	19.80	0.3
Thortveitite	2	0.5
Var. "Befanamite"	1.3	1.0
Wöhlerite	15.61	0.5
Zircon	64.23	0.98
Hyacinth	64.83	1.2
Var. Hagatalite[2]	39.5	2.5
Oyomalite[2]	38.4	2.5
Alvite	41.98	4.6
Alt. Cyrtolite	52.4	5.5
Malacon	53.2-65.18	3.4-2.6
Naegite	49.8	3.5
Zirkelite	51.89	1.0

[1] Lee, O. Ivan, Work cited, p. 22.

[2] Kimura, K. Zeit. Phys. Chem. vol. 128, 1927, p. 396.

List of zirconium minerals not reported investigated for hafnium[1]

Name	Per cent of ZrO_2
Astrophyllite	1.21-4.97
Beckelite	2.5
Chalcolamprite	5.71
Endeiolite	3.78
Guarinite) Identical?	19.70
Hiortdahlite)	21.48
Johnstrupite	2.84
Lavenite	28.79-28.90
Leucosphenite	3.5
Loranskite (var. wiikite)	20.00
Lorenzenite (ramsayite)	11.92
Mosandrite	7.43
Nohlite (var. samarskite)	2.96
Oliveiraite (alt. euxenite)	63.36
Orvillite (in zircon in "caldasite")	68.04
Riebeckite (arfvedsonite)	0.75-4.7
Soda-catapleite (var. catapleite)	30.80
Uhligite	21.95
Zircon	
Alt. Auerbachite	38-61.53-69

[1] Lee, O. Ivan, Work cited, p. 24.

IDENTIFICATION AND ANALZSIS[10]

Although, for authentic determination of the actual hafnium content of minerals and ores, reliance must for some time to come be placed on experienced chemists, the radioactivity of the mineral might aid in preliminary identification and even in an approximate estimation in the case of the different varieties of zircon and its alteration minerals. As different types of altered zircon that have been found to be richest in the new element are pseudomorphic after zircon, it is not difficult to recognize their square pyramidal form, if specimens of various alterations are studied. If such minerals, upon identification as zircons, exhibit pronounced radioactivity, it may be assumed that they contain appreciable quantities of hafnia.

Any chemical reaction that is characteristic of zirconium can be used to identify hafnium also, as, for example, the precipitation of phosphates insoluble in concentrated mineral acids, the coloring of tumeric paper, and so on. As hafnium is always associated with zirconium in nature, the practical analytical problem in dealing with the new element is to determine the hafnium content of zirconium preparations. When such preparations are quite pure, their hafnium content can be readily determined (1) by density measurements or (2) by analysis of any well-defined compound (e.g., one of the double fluorides, the sulphate, or one of the tetrafluorides). But if impurities are present, the method of quantitative X-ray spectroscopy has to be applied.

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[10] Lee, O. Ivan, Work cited, pp. 24 and 35.

GEOGRAPHICAL DISTRIBUTION

In general, any discussion of the deposits of zirconium covers deposits of hafnium as well. Reference, therefore, is made to the Bureau of Mines information circular on zirconium deposits. A tabulated summary of hafnium mineral occurrences follows:[11]

The occurrence of hafnium minerals by countries[1]

Locality	Mineral	ZrO_2	HfO_2
Africa:			
Diego Suarez	Zircon		0.8
Madagascar	Zircon		0.9
Madagascar	Grey zircon		0.8
Madagascar, Befanamo	"Befanamite," (thortveitite)	1.3	1.0
Madagascar	Malacon (alt. zircon)	53.2	4.
Asia:			
Ceylon	Beccarite (var. zircon)		2.1
Ceylon	Reddish-brown zircon		2.7
Ceylon	Zirkelite	51.89	1.
India (Travancore?)	Zircon from monazite	64.0	1.2
Japan, Naegi Mino Prov.	Naëgite	48.30	7.
Japan, Naegi Mino Prov.	Naëgite	49.8	3.5
Siam, Province of Chantaboon	Zircon (transparent blue)		4.?
Australia: No minerals have yet been definitely reported from the continent as containing hafnium			
Tasmania	Zircon		(2)
Tasmania	Greyish brown zircon		1.1
Europe:			
Austria, Carinthia	Zircon (transparent white)		4.?
France, Espailly (Le Puy)	Zircon (var. hyacinth; transparent red)	64.83	1.2
France, Espailly (Le Puy)	Zircon (var. hyacinth; transparent red)		0.7
France, Espailly (Le Puy)	Zircon (transparent green)		1.1
Italy, Lonedo	Zircon (yellow)		0.7
Italy, Lonedo	Zircon (red)		0.7
Italy, Vicenza	Zircon (transparent green)		0.8
Italy, Vesuvius	Zircon		0.7
Norway, Barkevik	Eudialyte (var. eucolite)	14.47	0.7
Norway, Barkevik	Eudialyte (var. eucolite)	12.21	0.2
Norway, Barkevik	Wöhlerite	15.61	0.5
Norway, Brevik	Zircon		1.0
Norway, Brevik	Reddish-brown zircon	63.2	1.0
Norway, Frederiksvärn	Polymignite	29.11	0.6

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[11] Lee, O. Ivan, The Mineralogy of Hafnium: Chem. Rev., vol. 5, No. 19, 1928, pp. 32-34.

The occurrence of hafnium minerals by countries - Continued

Locality	Mineral	ZrO_2	HfO_2
Europe - (Continued:			
Norway, Frederiksvärn	Brown zircon	65.2	1.0
Norway, Gjersted	Alvite (alt. zircon)		9.
Norway, Iveland	Thortveitite	2	0.5
Norway, Hitterö	Malacon (alt. zircon)	65.18	2.6
Norway, Kragerö	Alvite (alt. zircon)	41.98	4.6
Norway, Kragerö	Alvite (alt. zircon)		3.
Norway, Kragerö	Alvite (alt. zircon)		8.
Norway, Kragerö	Alvite (alt. zircon)		15.
Norway	Catapleite	31.52	0.3
Norway, Langesund	Brown zircon		1.7
Norway, Langesund	Rosenbuschite	19.80	0.3
Norway, Larvik	Greyish brown zircon		6.
Norway, Risör	Alvite (alt. zircon)		10.
Norway	Grey syenite (rock)		3.8
Norway, Unneland	Thortveitite	0.8	1.1
Sweden, Alno	Pyrochlore	2.90	Trace
Russia, Miask	Greyish brown zircon	64.22	1.1
Russia, Rojkow Kliutsch, Ural	Brown zircon		0.5
Russia, Kola	Eudialyte (red)		0.1
North America:			
Canada, Eganville, Ont.	Brown zircon		1.2
Canada, Renfrew County, Ont.	Zircon		0.6
Canada, Henvey Tp., Parry Sound District, Ont.	Cyrtolite, black (alt. zircon)		2.11
Greenland	Zircon		0.8
Greenland	Catapleite	31.53	0.3
Greenland, Narsarsuk	Elpidite	20.28	0.2
Greenland, Narsarsuk	Reddish-brown zircon		0.8
Greenland, Narsarsuk	Eudialyte (red)	12.20	0.2
Greenland, Narsarsuk	Eudialyte (brown)	12-16	0.6
Greenland, Kangerdluarsuk	Eudialyte	14.32	0.17
United States, Connecticut	Zircon		1.0
United States, Rockport, Mass.	Cyrtolite (alt. zircon)	40.	9.
United States, Rockport, Mass.	Cyrtolite (alt. zircon)	44.	17.(?)
United States, Bedford, N. Y.	Cyrtolite (alt. zircon)	52.4	5.5
United States, N. Car.	Grey zircon		4.(?)
United States, N. Car.	Brown zircon		1.3
United States, Henderson Co., N. Car.	Zircon		4.0(?)
Oceania: No minerals have yet been reported definitely as containing hafnium			
South America:			
Brazil	Baddeleyite	97.7	1.2
Brazil	Fava	92.42	0.7
Brazil	Fava (shell)	59.	0.5
Brazil	Fava (nucleus)	74.	0.5
Brazil	Zircon separated from monazite sand	64.	0.4
Brazil, Caldas	Zircon		1.8
Brazil, Minas Geraes	Zircon		1.0

1 Lee, O. Ivan, Work cited, pp. 32-34. 2 "Very considerable."

The richest hafnium ores are the altered zircons (especially cyrtolite). The unaltered zircons, the native oxide (baddeleyite) and eudialyte, being more abundant are the more important of the leaner hafnium ores.

United States.- Unaltered zircon (the only commercial hafnium ore in the United States), which usually contains less than 2 per cent of hafnium oxide, has been mined intermittently in Henderson County, N. C., and at Pablo Beach, Fla., and has been reported in Virginia, near Ashland. It also has been found near Indiahoma, Commanche County, Okla. Baddeleyite has been reported in Montana, and eudialyte has been found in Arkansas.

Of the altered zircons, cyrtolite, which is the most widely distributed, occurs in at least eight States, as follows:

California (Southern).
Colorado, Mount Antero.
Connecticut, Branchville.
Massachusetts, Rockport.
New York, Westchester County, near Bedford.
North Carolina, Mitchell and Henderson
  Counties (three localities).
Pennsylvania (five localities).
Texas, Llano.

The cyrtolite at Rockport (Mass.) probably contains as much as 17 or even 20 per cent hafnium, but this ore is very rare, as it is in Connecticut and Colorado also. As a 24-hour exposure of the cyrtolite of Texas yielded good radiographs, it is assumed that this ore likewise is high in hafnia, although no analysis has been reported. It is stated that cyrtolite was abundant in the famous Baringer Hill locality when the yttria minerals were being mined there. The radioactive cyrtolite of New York, which is as abundant as that of Texas, is unusually high in hafnia and appears to be the most promising domestic source of supply. A large feldspar mine situated near Bedford in the hills of Westchester County, within about 40 miles of New York City, has yielded a variety of unusual mineral specimens. Among these minerals was cyrtolite, which had been known for some time to contain a small percentage of uranium and probably rare earths. Mr Lee sent a sample of this mineral to Prof. C. James of the University of New Hampshire, who reported the presence of some 10 per cent of hafnia in the mixed oxides (HfO_2 and ZrO_2). James's original analysis was confirmed by Hevesy, who found approximately 9.5 per cent of hafnium oxide in the mixed zirconium oxides, which totalled 52.44 per cent. These unusually high percentages of hafnia appear to be rather consistently maintained in different samples from this locality, although the yttria earths content varies considerably. The deposit is not large, but specimens weighing 10 or 12 pounds are not uncommon; and Professor James actually worked up a fairly large quantity of this material for hafnium and its associated zirconium.[12]

Foreign countries.- Of the ores richest in hafnia, the altered zircon, cyrtolite, occurs in India, Madagascar, Italy, Sweden, and Canada (Hybla and Parry Sound district, Ontario). Alvite, which does not seem to be common but which was useful to early investigators of hafnium, occurs in Norway.

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[12] Lee, O. Ivan, Work cited, pp. 25-29.

Of the ores lean in hafnia, the zircon of commerce has come from the monazite sands of Travancore, India, and of Brazil, and from the pegmatites of southern Norway.

Baddeleyite (the native oxide), known for 37 years, occurs in Ceylon, Italy, Sweden, and especially in Brazil, in the States of Minas Geraes and São Paulo. Bowlders in the Brazilian deposit have been found that weighed as much as 30 tons; such bowlders would probably contain 300 to 400 pounds of hafnium oxide.

The complex eudialyte, said to be a third hafnium mineral of great interest, is reported to be very abundant in Hibina-Toundra and Lujavr-urt, in the Kola Peninsula of Russian Lapland. (Although specimens of about a dozen others of the rarer zirconium minerals have been collected from the same region, only the eudialyte has been analyzed for hafnium.) Eudialyte is reported to be of common occurrence in the alkaline syenites in Greenland, about the fiords of Tunugdliarfik and Kangerdluarsuk, in the Julianehaab district.

HISTORY

D. Coster and G. von Hevesy are credited with the discovery of hafnium. They made their announcement on January 2, 1923,[13] after measuring the X-ray spectra of a number of zirconium minerals and finding some characteristic lines in the L-series belonging to no previously known element. The X-ray method was used for the quantitative determination of hafnium by comparing the intensities of the lines of a known amount of the neighboring element tantalum (number 73 in the periodic table) with those of the unknown element.

After the discovery of hafnium there was some controversy following the claim by G. Urbain that the new element was identical with that which he had described as "celtium" in 1911 and which he had found in some residues remaining after the separation of the lutecium-ytterbium fractions of the rare earths. However, the existence of "celtium" as a new element was later disproved.[14] Dr. Alexander Scott, likewise, was considered as a possible claimant of the honor of discovering the new element. In 1913 he stated that in analyzing samples of a black sand from New Zealand he had extracted a cream-colored sand containing about 75 per cent titanium oxide and also a highly refractory residue which he considered a new oxide. Coster and Hevesy, however, after examining some of the material sent them by Doctor Scott informed him that it failed to yield any hafnium lines in the spectrum. A complete discussion of their findings, showing that the so-called "element celtium" was widely different from hafnium, particularly in its chemical reactions, was made by Coster and Hevesy[15] soon after the original announcement of their own discovery; and two years later Hevesy[16] summarized the various attempts to find new elements in zirconium minerals since zirconium itself was identified by Klaproth in 1789, as follows:

> In 1845 Svanberg expressed the view that zirconium minerals contained an element similar to zirconium, which he named norium. Sjögren, another Swedish chemist, a few years later, again thought he had found Svanberg's norium in the zirconium mineral catapleiite. Then came Nylander's announcement (1869) of the discovery of jargonium, an

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[13] Coster, D., and Hevesy, G., On the Missing Element of Atomic Number 72: Nature, vol. 111, London, Jan. 20, 1923, p. 79.

[14] Mellor, J. W., Work cited, p. 166.

[15] Coster, D., and Hevesy, G., On the New Element Hafnium: Nature, vol. 111, London, Feb. 24, 1923, p. 252.

[16] Hevesy, G., The Discovery and Properties of Hafnium: Chem. Rev., vol. 2, No. 1, April, 1925, pp. 10-11.

> element similar to zirconium, but having a lower atomic weight; and in the same year Church thought he had discovered the new element nigrium. We may add to this list the announcement of Ogawa (nipponium, 1908), and of Hoffmann and Prandtl (1901), who believed they had found a new earth ("euxen earth") in the mineral euxenite. The genuineness of all these announcements was later disproved by different investigators, including Marignac, Weibull, and Hauser, who showed the identity of norium, and so on, with zirconium. Most of these announcements were made on the basis of peculiar chemical reactions believed not to be characteristic of zirconium, and from this fact alone we can straightway conclude that the above announcements have nothing to do with the presence of hafnium, as zirconium and hafnium show the same chemical reactions. Nevertheless, the latter element was without exception undoubtedly present in the investigated samples.

SEPARATION OF ZIRCONIUM AND HAFNIUM

A number of methods that Coster and Hevesy [17] have described for the separation of zirconium and hafnium include fractional crystallization or precipitation of (1) zirconium and hafnium sulphates, (2) fluorides or double fluorides, (3) oxalates in presence of fluorides, (4) hydroxides, (5) oxyhalides, and (6) organic compounds.

The methods of Van Arkel and De Boer[18] for the separation of zirconium and hafnium depend upon (1) fractional precipitation of oxalates from solutions free of fluorides, (2) adding phosphorus pentachloride to mixed hafnium and zirconium halides and fractional distillation, (3) adding zirconium and hafnium mixture to concentrated sulphuric acid and fractional precipitation by means of a base, and (4) by fractional precipitation with hydrogen peroxide and organic compounds.

A recent German patent[19] covers the separation by the fractional crystallization, sublimation, and precipitation of their halogen compounds (except fluorides); special mention is made of the oxychlorides, due to their difference in solubility.

PREPARATION OF HAFNIUM AND ZIRCONIUM

A method for the preparation of pure zirconium and hafnium, which is a summary made by Marden[20] of an article by Van Arkel and De Boer,[21] follows:

> Their process consists in heating zirconium or hafnium tetraiodide in a pyrex bulb to 600° C. The bulb contains, in addition to the chemical compounds, a tungsten filament heated to 2,000° C. The

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[17] Coster, Dirk, and von Hevesy Georg, Separation of Hafnium and Zirconium: Canadian Patents 275682 to 275687, incl. (to N. V. Philips' Gloeilampenfabricken, Eindhoven, The Netherlands), Nov. 22, 1927.

[18] De Boer, Jan Hendrik, Separation of Hafnium and Zirconium: Canadian Patents 275692 and 275695 (to N. V. Philips' Gloeilampenfabricken), Nov. 22, 1927.
Van Arkel, A. E., and De Boer, Jan Hendrik Separation of Hafnium and Zirconium: Canadian Patents 275688, 275691, 275693, and 275694 (to N. V. Philips' Gloeilampenfabricken), Nov. 22, 1927.

[19] Ger. Pat. 492754, vide Foote-Prints, vol. 3, No. 2, 1930 pp. 334.

[20] Marden J. W., Titanium and Zirconium: Min. Ind., 1925, vol. 34, McGraw-Hill Book Co. (Inc.), 1926, p. 697.

[21] Van Arkel,________ and De Boer ________, ____________: Ztschr. anorg. Chem., vol. 148, 1925, p. 345.

tetraiodides vaporize at this temperature and dissociate when they come in contact with the tungsten filament at 2,000°, depositing the metal on the filament. It is claimed that it is possible to make filaments having a diameter of 2 to 4 millimeters in thickness and that these metals when made in this way are extremely soft and pliable, resembling copper.

PREPARATION OF PURE HAFNIUM SALTS[22]

A 60 per cent hafnium salt prepared by the hydrofluoric acid-borax process was dissolved in hydrofluoric acid, precipitation was brought about with sodium hydroxide, the precipitate was washed free from fluoride, phosphate and borate, and dissolved in hydrochloric acid. By treatment of this precipitate according to the sulphuric acid method of separation, a 100 per cent hafnium fraction was obtained on the second treatment. Hafnium phosphate may be converted into the hydroxide by treatment with hydrofluoric acid and potassium hydroxide, solution in hydrochloric acid, and precipitation by ammonium hydroxide. Contamination with silicic acid from hydrofluosilicic acid in the hydrofluoric acid may be removed by evaporating the hydrofluoric acid solution to dryness and taking up with hydrochloric acid. After removal of silica the hydrochloric acid solution is evaporated; crystallization and recrystallization give the oxychloride $HfOCl_2.8H_2O$. Washing with alcoholic hydrochloric acid removes iron salts. The hydrochloric acid should not be too concentrated, because of the tendency to form a complex hafnium chloro acid. Ignition yields white oxide of hafnium.

PRODUCTION AND TRADE

The first hafnium salts produced in the United States were made by the late Prof. C. James of the University of New Hampshire in 1924 from cyrtolite from near Bedford, N. Y. However, although the zirconium salt which he prepared concomitantly appears to have been free from hafnium, the hafnium salt was unfortunately contaminated in process by zirconium through the interchange of fractions by careless workmen who had access to the laboratory. To date, therefore, pure hafnium salts have apparently not been prepared in the Western Hemisphere. Apparently the metal likewise has not been produced in this country, but a small sample of the first metallic hafnium ever made was presented by G. Hevesy for permanent exhibition in the element collection being made by Dr. George F. Kunz at the American Museum of Natural History in New York City.

Practically all the hafnium and its compounds that have been isolated so far have been consumed in scientific and experimental work, and production has of course been confined to a small laboratory scale. In 1930, however, de Boer and Fast are said to have prepared some 70 grams of 100 per cent hafnium oxide from which they made some pure, ductile metal, as well as a series of hafnium-zirconium alloys.

Domestic supplies are imported and may be obtained through various dealers in rare metals and chemicals, as for example:

Foote Mineral Co., (Inc.), 1609 Summer St., Philadelphia, Pa.
A. D. Mackay, 26 Cortlandt St., New York, N. Y.

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[22] de Boer, J. H., and Broos, J., Ztschr. anorg. allgem. Chem., vol. 187 (1930), p. 190; Foote-Prints, vol. 3 (1930) No. 2, p. 34.